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(54) Degradable foam, process for its preparation and use of same

Abbaubarer Schaum, Verfahren zu seiner Herstellung und seine Verwendung Mousse dégradable, procédé pour son préparation et son utilisation

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Description

The present invention relates to a degradable foam and a method for its production. More particularly, the invention relates to a foam which is composed of a thermoplastic polymer composition substantially comprising polylactic acid or a copolymer of lactic acid and hydroxycarboxylic acid and has degradable characteristics in the natural environment.

The foam of these thermoplastic and degradable polymers can be used for food containers and throwaway cups after processing into sheets or used for heat insulating materials or cushioning materials in the form of bulk.

Foams of polyolefin, polyurethane and polyamide based resin have been conventionally used in a broad field of containers, cushioning materials and heat insulating materials. These foams, in particular, can be processed into formed articles with a small amount of resin and hence are used for food containers, disposable cups and lunch boxes which are cheap and light and also for interior dividers and wrapping materials of readily damageable matters such as vegetables, fruits and perishable foods.

However, the foams prepared from these resins or articles such as containers, cushioning materials and heat insulating materials which are prepared from these foams are of great bulk on discarding and increase amount of garbage. Additionally, conventional products have very slow degradation speed in the natural environment and remain semipermanently when disposed under the ground. Further, throw away plastics have caused problems such as damage of a view and destruction of the living environment of marine organisms.

However, the foams capable of readily degrading in the natural environment and articles such as containers, cushioning materials and heat insulating materials obtained by using these foams have not yet been known.

On the other hand, a lactic acid-based polymer, that is, a polymer substantially consisting of lactic acid or a copolymer of lactic acid has been known as a thermoplastic and degradable polymer.

The lactic acid-based polymer has degradable characteristics in the natural environment. When the polymer is allowed to stand in soil or sea water, the polymer starts degradation within several weeks and disappears in about a year. Final degradation products are lactic acid, carbon dioxide and water. All of these products are non-hazardous.

The raw material lactic acid can be obtained by fermentation of inexpensive materials such as corn starch and corn syrup and can also be prepared from petrochemicals such as ethylene.

USP 1,995,970 discloses a preparation process by polymerization of lactic acid, lactide or a mixture of these compounds. Polymers of lactic acid are usually prepared from a cyclic dimers of lactic acid, called lactide. The polymers can also be directly prepared from lactic acid through dehydrating condensation. The straight chain polyester prepared from lactide by ring-opening polymerization has a high molecular weight. On the other hand, the polymer directly obtained from lactic acid by dehydiating condensation is liable to difficultly increase molecular weight even through reaction time is extended.

The lactic acid-based polymer has been used for surgical sutures and medical slow release matrixes because of good biological compatibility and degrading ability. However, foams of the polymer which are used for containers, heat insulating materials and cushioning materials have not yet been known.

It is desirable that embodiments of the invention provide a foam of a thermoplastic and degradable polymer which can degrade with ease in the natural environment and does not impair the natural environment, and to provide a container and cushioning material obtained by using the foam.

The present inventors have found out that a lactic acid-based polymer can be foamed without impairing the degradable characteristics of the polymer and additionally that the resulting foam has excellent physical properties such as heat insulation and mechanical strengths.

In a first aspect of the present invention there is provided a method for the preparation of a degradable foam, the method comprising foaming a thermoplastic polymer composition comprising polyactic acid or a copolymer of lactic acid and hydroxycarboxylic acid with a foaming agent thereby to generate numerous cells dispersed through the polymer, said polyactic acid or copolymer having a degree of polymerisation in the range 150 to 20,000 the foaming agent being selected from (1) decomposition type foaming agents; and (2) evaporation type foaming agents selected from the group consisting of ethane, propane, butane, pentane, hexane, heptane, ethylene, propylene and petroleum ether.

In other aspects there is provided a degradable foam as obtainable by the method of the first aspect; a container prepared from the degradable foam; and a cushioning material prepared from the foam.

Polylactic acid or a copolymer of lactic acid and hydroxycarboxylic acid for use in the invention may be prepared by using lactic acid or lactide, namely a cyclic dimers of lactic acid, and hydroxycarboxylic acid as raw materials.

Exemplary hydroxycarboxylic acid includes glycolic acid, hydroxybutyric acid, hydroxyvaleric acid, hydroxypentanoic acid, hydroxycaproic acid and hydroxyheptanoic acid. Specially, glycolic acid, 3-hydroxylactic acid, 4-hydroxylactic acid, 3-hydroxyvaleric acid or 6-hydroxyl caproic acid is used preferably. In certain cases, other monomers can be suitably used as a mixture.

The lactic acid polymer used for the invention may be prepared directly from lactic acid by dehydrating polycondensation or may be prepared by ring-opening polymerization of lactide.

When a low molecular weight polymer is permitted, polymer may be obtained by dehydrating condensation of lactic

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acid. When a high molecular weight polymer is required, polymer is preferably obtained by ring-opening polymerization of lactide.

Lactides which can be used for the ring-opening polymerization are L-lactide, D-lactide, meso-lactide and a mixture of these lactides. A mixture of D- or L-lactide with a lactide having opposite optical activity is preferred. Preferred mixing ratio is D- or L-lactide/optical antipode = $95/5 \sim 50/50$.

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Polymerization degree of lactic acid-base polymer is in the range of from 150 to 20,000. Polymerization degree lower than the range leads to low mechanical strengths of processed articles such as films and is unsuitable for practical use.

Polymerization degree higher than the range results in high melt viscosity and inferior processing ability. Polymerization can be carried out in the presence or absence of a solvent. In view of solvent recovery problem, bulk polymerization without solvent is preferred in industry.

A process for preparing lactic acid-based polymer by ring-opening polymerization of lactide and glycolide will be exemplified hereinafter.

The ring-opening polymerization is carried out in the presence of a catalyst. Catalysts which can be used are generally chloride or carboxylate of zinc or tin and include, for example, stannous octoate, tin tetrachloride, zinc chloride, titanium tetrachloride, iron chloride, boron trifluoride ether complex, aluminium chloride, antimony trifluoride, lead oxide and other multi valent metal containing compounds. No particular restriction is imposed upon the polyvalent metals. Tin compounds and zinc compounds are preferably used. However, in the case of using for biocompatible materials and food products, these metals must be selected in view of toxicity.

The amount of the catalyst used is preferably in the range of from 0.001 to 0.1 % by weight for lactide or for the total weight of lactide and glycolide.

Known chain extenders can be used for the polymerization. Preferred chain extenders are higher alcohols such as lauryl alcohol and hydroxy acids such as lactic acid and glycolic acid. Polymerization rate increases in the presence of a chain extender and polymer can be obtained within a short time. Molecular weight of the polymer can also be controlled by variating the amount of the chain extender. However, too much amount of the chain extender tends to decrease molecular weight of polymer formed. Hence, the amount of the chain extender is preferably 0.1 % by weight or less for lactide or for the total weight of lactide and glycolide.

Polymerization or copolymerization can be carried out in the presence or absence of a solvent. Bulk polymerization in a molten state of lactide or glycolide is preferably carried out in order to obtain high molecular weight polymer.

In the case of molten polymerization, polymerization temperature may be generally above the melting point (around 90 °C) of the monomer, lactide or lactide and glycolide. In the case of solution polymerization which uses solvents such as chloroform, polymerization can be carried out at temperature below the melting point of lactide or lactide and glycolide. In any case, polymerization temperature above 250°C is unfavorable because decomposition of formed polymer develops.

The foam of the invention is formed in such structure that a great many cells are dispersed throughout the polymer. Foaming of the polymer can be carried out with an optional method. A method using a foaming agent is usually preferred because the method can be carried out cheaply with ease. Foaming is preferably carried out in the processing step. Preferred processing method is so-called extrusion foaming where foam expansion takes place simultaneously with delivery from an extruder.

Foaming agents which can be used are decomposition type foaming agents which generate gas by decomposition on heating, and include, for example, inorganic foaming agents such as sodium hydrogen carbonate and organic foaming agents such as azodicarbonamide, N,N'-dinitrosopentamethylenetetramine, p,p'-oxybis(benzenesulfonylcarbazide), azobisisobutyronitrile and benzenesulfonylhydrazide.

Similarly, evaporation type foaming agents which generates cells by vaporization of liquid can also be used, and are selected from ethane, propane, butane, pentane, hexane, heptane, ethylene, propylene and petroleum ether.

The amount of the foaming agent is preferably from about 0.1 to about 30% by weight, more preferably from about 0.5 to about 10% by weight for the polymer composition. Auxiliary foaming agents, cell stabilizers and nucleating agents can also be added in a suitable amount, if desired, and include, for example, organic acids such as stearic acid, oxalic acid, salicylic acid, phthalic acid, benzoic acid, citric acid and tartaric acid; inorganic acids such as boric acid; salts of these organic and inorganic acids; carbonates such as sodium carbonate; zinc oxide, calcium oxide, titanium oxide, silica, alumina, clay, kaolin and diatomaceous earth.

In preparing the foam, plasticizers can also be added to the polylactic acid-based polymer composition in order to provide flexibility for the foam.

Plasticizers which can be safely used for wrapping and containers of foods are preferably added in preparation of the foam and include, for example, diethyl phthalate, dioctyl phthalate, dicyclohexyl phthalate and other phthalic acid esters; di-i-butyl adipate, di-n-octyl adipate, di-n-butyl sebacate, di-2-ethylhexyl azelate and other aliphatic dicarboxylic acid esters; diphenyl 2-ethylhexyl phosphate, diphenyl octyl phosphate and other phosphoric acid esters; tributyl acetylcitrate, tri-2-ethylhexyl acetylcitrate, tributyl citrate and other hydroxypolycarboxylic acid esters; methyl acetylrici-

noleate, amyl stearate and other aliphatic esters; glycerol triacetate, triethylene glycol dicaprylate and other polyhydric alcohol esters; epoxylated soybean oil, octyl epoxystearate and other epoxy-base plasticizers; and polypropylene glycol adipate, polypropylene glycol sebacate and other polyester base plasticizers.

The amount of the plasticizer added is usually from about 5 to about 50% by weight, preferably from about 5 to about 20% by weight for the polymer composition, the plasticizer is added as a solution in a solvent to the lactic acid-base polymer or may be added in molten state.

Pigments, flame retardants and fillers can be added in a suitable amount in order to color or modify foamed articles.

Foaming temperature differs depending upon the polymer composition. Foaming is usually carried out at temperature where melt viscosity is maintained in the range of from about 30,000 to about 80.000 poise. When the temperature is lower than this range, molten polymer has high viscosity, formation of cells is slow, and thus foaming rate is low. On the other hand, when the temperature is higher than this range, viscosity of the polymer becomes too low, retention of cells becomes difficult and thus the resultant foam is collapsed.

Foaming rate differs depending upon the object for use. Foaming rate of about 1.5 to about 20 times is preferred for food packaging trays and throw away cups which require mechanical strengths. In the case of using for heat insulating materials and cushioning materials which require relatively low mechanical strengths, foaming rate is preferably about 3 to about 50 times, more preferably about 5 to about 25 times.

In order to use the foam of the invention for a container, a foamed sheet obtained by extrusion foaming is heated again, softened and successively hot molded into a desired shape by vacuum or press molding. The foamed container preferably has a partially removed skin layer on the outside surface.

In order to partially remove the skin layer from the outside surface, for example, cut lines are fitted on the surface layer of the sheet foam prior to hot molding and enlarged by heating in an oven before molding the container. Alternatively, the container is perforated after molding.

In cases where the foam of the invention is used for a cushioning material, a sheet foam or a net-shaped foam is used singly or as a lamination with paper. Good cushioning performance can be obtained by the method without impairing degradable characteristics of the foam in the invention.

The sheet foam can be softened by heating again and successively hot molded into a desired form by vacuum or press molding. Preferred sheet foam is partially perforated to install many edge faces in the sheet.

The net-shaped foam can be cut into a prescribed length and used by bringing into contact with an article to be wrapped. Alternatively, the net-shaped foam can be used for a divider or an underlay pad by laminating with paper.

The present invention will hereinafter be illustrated in detail by way of examples. However, these examples are not intended to limit the scope of the present invention.

Examples 1~3 (Comparative)

To a mixture of poly D,L-lactide having a molecular weight of 100,000 and poly L-lactide, 0.5% by weight of talc was added as a cell regulator as illustrated in Table 1. The resulting mixture was melt-kneaded with an extruder having an internal diameter of 50 mm. Successively, dichlorodifluoromethane was charged under pressure at a ratio of 0.065 mole per 100g of the resin, delivered at 140°C through a slit into the atmosphere to obtain a sheet foam. Thickness and apparent density of the sheet foam obtained are illustrated in Table 1.

A test specimen having dimensions of 10X 50 mm was cut out of the sheet foam and a degradation test was conducted in warm water at 60°C. Results are illustrated in Table 1.

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Example	1	2	3	
L-PLA (wt%)	80	50	20	
DL-PLA (wt%)	20	50	80	
Sheet thickness (mm)	1.1	2.5	2.6	
Density (g/cc)	0.48	0.30	0.26	
Flexural modulus (kgf/cm ²)	200	5500	4100	
Thermal conductivity λ (kcal/m.h.°C)	0.06	0.05	0.04	
Weight loss in warm water (60 °C, 20 days) (%)	8	11	14	

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Examples 4-6

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To a copolymer of L-lactide and oxycarboxylic acid, 1.5% by weight of azodicarbonamide was dry blended as illustrated in Table 2. The mixture was melt-kneaded with a 500 mm Ø extruder and delivered through a slit at 140 °C into the atmosphere to obtain a sheet foam. Thickness and apparent density of the sheet foam are illustrated in Table 2. The same degradation test as in Example 1 was carried out in warm water and results are illustrated in Table 2.

Table 2

Example	4	5	6	
L-Lactide (wt%)	50	50	50	
Comonomer	D-lactide	glycolide	ε-caprolactone	
Average molecular weight	100,000	100,000	70,000	
Sheet thickness (mm)	2.5	2.8	2.3	
Density (g/cc)	0.31	0.28	0.33	
Flexural modulus (kgf/cm²)	5,400	4,900	6,400	
Thermal conductivity (k cal/m.h.°C)	0.05	0.05	0.05	
Weight loss in warm water (60 °C, 20 days) (%)	16	18	23	

Examples 7 ~ 9

To a mixture of poly D,L-lactide having a molecular weight of about 100,000 and poly L-lactide, 0.5% by weight of talc was added as a cell regulator as illustrated in Table 3. The resulting mixture was melt-kneaded at 200 °C with a 50 mm ϕ extruder and successively butane was charged under pressure at a rate of 0.065 mole per 100g of the resin. Thereafter the resin mixture was cooled in the extruder to a cylinder temperature of 140 °C and delivered through a slit into the atmosphere to obtain a sheet foam having a width of 650 mm. Thickness and apparent density of the sheet foam thus-obtained are illustrated in Table 3. The sheet foam was vacuum molded into a tray having dimensions of 200×100×15 mm. Before entering into an oven of the vacuum molding machine, the sheet foam was passed through rolls so as to provide cross cuts of 5 mm in length for the outside surface of the tray. The cutting line was enlarged its width to about 2 mm after passing through the oven at 150°C. The sheet foam was successively placed on a mold and shaped by applying vacuum.

The skin layer was removed in the form of a lattice from outside of the tray thus obtained. The tray had no problem in practical use. Degradation test was carried out by burying the tray at 35°C into a soil having a moisture content of 30%. Evaluation of degrading characteristics was conducted by measuring weight loss. Results are summarized in Table

3.

40 Examples 10~12

Sheet foam and tray were prepared by carrying out the same procedures as described in Example 7 except that a copolymer of L-lactide and hydroxycarboxylic acid was used. Thickness and apparent density of the sheet foam and results of degradation test are illustrated in Table 4.

Table 3

Example	7	8	9	
L-PLA (wt%)	80	50	20	
DL-PLA (wt%)	20	50	90	
Sheet thickness (mm)	1.1	2.5	2.6	
Density (g/cc)	0.14	0.10	0.09	
Weight loss in soil (35°C, 20 days) (%)	8	11	14	

Table 4

Example	10	11	12
L-Lactide (wt%)	50	50	50
Comonomer	D-lactide	glycolide	ε-caprolactone
Average molecular weight	100,000	100,000	70,000
Sheet thickness (mm)	2.5	2.8	2.3
Density (g/cc)	0.09	0.08	0.10
Weight loss in soil (35°C, 20 days) (%)	16	18	23

Examples 13~15

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To a mixture of poly D,L-lactide having a molecular weight of about 100.000 and poly L-lactide as illustrated in Table 5, 0.5% by weight of talc was added as a cell regulator and melt-kneaded with a 50 mm @ extruder at 200°C and successively butane was charged under pressure at a rate of 0.065 mole per 100g of the resin. Thereafter the resin mixture was cooled by maintaining the cylinder temperature of the extruder at 140~175°C and delivered through a slit into the atmosphere to obtain a sheet foam having a thickness of 2~3 mm and a width of 650 mm. The cushioning property of the sheet foam obtained was evaluated by dropping a steel ball of 5/8 from a height of 46 cm to the sheet foam and measuring the rebound height in accordance with JIS K-6382. Apparent density and cushioning property are illustrated in Table 5.

The degradation test was conducted by burying the sheet foam at 35°C into a soil having a moisture content of 30%. Result were evaluated by weight loss and are shown in Table 5.

Table 5

Example	13	14	15
L-PLA (wt%)	80	50	20
DL-PLA (wt%)	20	50	90
Cushioning property (%)	28	26	22
Density (g/cc)	0.14	0.10	0.09
Weight loss in soil (35°C, 20 days) (%)	8	11	14

Examples 16~18

Sheet foam was prepared by carrying out the same procedures as described in Example 13 except that copolymers of L-lactide and hydroxycarboxylic acid were used as illustrated in Table 6.

Table 6

Example	16	17	18
L-Lactide (wt%)	50	50	50
Comonomer	D-lactide	glycolide	ε-caprolactone
Average molecular weight	100.000	100.000	70.000
Cushioning property (%)	21	20	24
Density (g/cc)	0.09	0.08	0.10
Weight loss in soil (35°C, 20 days) (%)	16	18	23

Claims

1. A method for the preparation of a degradable foam, the method comprising foaming a thermoplastic polymer com-

position comprising polylactic acid or a copolymer of lactic acid and hydroxycarboxylic acid with a foaming agent thereby to generate numerous cells dispersed through the polymer, said polylactic acid or copolymer having a degree of polymerisation in the range 150 to 20 000 the foaming agent being selected from (1) decomposition type foaming agents; and (2) evaporation type foaming agents selected from the group consisting of ethane, propane, butane, pentane, hexane, heptane, ethylene, propylene and petroleum ether.

- A method according to claim 1 wherein the foaming agent is a decomposition type foaming agent generating carbon dioxide or nitrogen gas by decomposition on heating.
- 3. A method according to claim 2 wherein the foaming agent is selected from sodium hydrogen carbonate, azodicarbonamide, N,N'-dinitrosopentamethylene tetramine, p,p'-oxybis (benzenesulfonylcarbazide), azobisisobutyronitrile and benzenesulfonylhydrazide.
 - 4. A method according to claim 1 wherein the foaming agent is an evaporation type foaming agent.
 - 5. A degradable foam as obtainable by the method of any one of claims 2 to 4.
 - **6.** A degradable foam according to claim 5 wherein the polymer composition consists substantially of polylactic acid or a copolymer of lactic acid and hydroxy carboxylic acid.
 - 7. The degradable foam of claim 5 or claim 6 wherein the lactic acid is L-lactic acid, D-lactic acid or a mixture of L-and D-lactic acids.
- 8. The degradable foam of any one of claims 5 to 7 wherein the hydroxycarboxylic acid is glycolic acid, 3-hydroxylactic acid, 4-hydroxylactic acid, 4-hydroxylactic acid, 5-hydroxylactic acid, 6-hydroxycaproic acid or mixture thereof.
 - 9. A container prepared from the degradable foam of any one of claims 5 to 8.
 - 10. A cushioning material prepared from the degradable foam of any one of claims 5 to 8.

Patentansprüche

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- 1. Verfahren zur Herstellung eines abbaubaren Schaums, wobei das Verfahren das Schäumen einer thermoplastischen Polymerzusammensetzung, die Polymilchsäure oder ein Copolymer aus Milchsäure und Hydroxycarbonsäure enthält, mit einem Schaumbildner umfaßt, um dadurch zahlreiche im Polymer verteilte Zellen zu erzeugen, wobei die Polymilchsäure oder das Copolymer einen Polymerisationsgrad im Bereich von 150 bis 20.000 aufweist, und wobei der Schaumbildner ausgewählt ist aus (1) Schaumbildnern vom Zersetzungstyp; und (2) Schaumbildnern vom Verdampfungstyp, die aus der Gruppe ausgewählt sind, die aus Ethan, Propan, Butan, Pentan, Hexan, Heptan, Ethylen, Propylen und Petrolether besteht.
 - 2. Verfahren nach Anspruch 1, worin der Schaumbildner ein Schaumbildner vom Zersetzungstyp ist, der beim Erhitzen durch Zersetzung Kohlendioxid oder Stickstoffgas erzeugt.
- 45 3. Verfahren nach Anspruch 2, worin der Schaumbildner aus Natriumhydrogenkarbonat, Azodikarbonamid, N,N'-Dinitrosopentamethylentetramin, p,p'-Oxybis(benzolsulfonylcarbazid), Azobisisobutyronitril und Benzolsulfonylhydrazid ausgewählt ist.
 - 4. Verfahren nach Anspruch 1, worin der Schaumbildner ein Schaumbildner vom Verdampfungstyp ist.
 - 5. Abbaubarer Schaum, wie nach dem Verfahren nach einem der Ansprüche 1 bis 4 erhältlich.
 - 6. Abbaubarer Schaum nach Anspruch 5, worin die Polymerzusammensetzung im wesentlichen aus Polymilchsäure oder einem Copolymer aus Milchsäure und Hydroxycarbonsäure besteht.
 - Abbaubarer Schaum nach Anspruch 5 oder 6, worin die Milchsäure L-Milchsäure, D-Milchsäure oder ein Gemisch aus L- und D-Milchsäuren ist.

- Abbaubarer Schaum nach einem der Ansprüche 5 bis 7, worin die Hydroxycarbonsäure Glykolsäure, 3-Hydroxymilchsäure, 4-Hydroxymilchsäure, 3-Hydroxyvaleriansäure, 6-Hydroxycapronsäure oder ein Gemisch daraus ist.
- 9. Aus dem abbaubaren Schaum nach einem der Ansprüche 5 bis 8 hergestellter Behälter.
- 10. Aus dem abbaubaren Schaum nach einem der Ansprüche 5 bis 8 hergestelltes Polsterungsmaterial.

Revendications

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- 1. Méthode de préparation d'une mousse dégradable, la méthode comprenant le moussage d'une composition de polymère thermoplastique comprenant de l'acide polylactique ou un copolymère d'acide lactique et d'acide hydroxycarboxylique avec un agent moussant pour ainsi générer de nombreuses cellules dispersées au travers du polymère, ledit acide polylactique ou copolymère ayant un degré de polymérisation dans l'intervalle de 150 à 20 000, l'agent moussant étant choisi parmi (1) des agents moussants du type à décomposition, et (2) des agents moussants du type à évaporation choisis dans le groupe consistant de l'éthane, du propane, du butane, du pentane, de l'hexane, de l'heytane, de l'éthylène, du propylène et de l'éther de pétrole.
- 2. Méthode selon la revendication 1, dans laquelle l'agent moussant est un agent moussant du type à décomposition générant le dioxyde de carbone ou du gaz azote par décomposition lors d'un chauffage.
 - 3. Méthode selon la revendication 2, dans laquelle l'agent moussant est choisi parmi llhydrogéno carbonate de sodium, l'azodicarbonamide, la N,N'-dinitrosopentaméthylène tétramine, le p,p'-oxybis (benzènesulfonylcarbazide), l'azobiisobutyronitrile et le benzènesulfonylhydrazide.
 - 4. Méthode selon la revendication 1, dans laquelle l'agent moussant est un agent moussant du type à évaporation.
 - 5. Mousse dégradable que l'on peut obtenir par la méthode selon l'une quelconque des revendications 2 à 4.
- 30 6. Mousse dégradable selon la revendication 5, où la composition de polymère consiste substantiellement en un acide polylactique ou un copolymère d'acide lactique et un acide hydroxycarboxylique.
 - 7. Mousse dégradable selon la revendication 5 ou la revendication 6, où l'acide lactique et l'acide L-lactique, l'acide D-lactique ou un mélange d'acides L- et D-lactique
 - 8. Mousse dégradable selon l'une quelconque des revendications 5 à 7, où l'acide hydroxycarboxylique est l'acide glycolique, l'acide 3-hydroxylactique, l'acide 4-hydroxylactique, l'acide 5-hydroxyvalérique, l'acide 6-hydroxyca-proique ou leur mélange.
- 9. Récipient préparé à partir de la mousse dégradable selon l'une quelconque des revendications 5 à 8.
 - Matériau d'amortissement préparé à partir de la mousse dégradable selon l'une quelconque des revendications
 à 8.